1960

Preparation and ultra-violet absorption studies of leucocyanides of the triarylmethane dyes

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PREPARATION AND ULTRA-VIOLET ABSORPTION STUDIES OF THE LEUCOCYANIDES OF THE TRIARYLMETHANE DYES

A Thesis

Submitted to

the Faculty of the College of the Pacific

In Partial Fulfillment

for the Degree of Master of Science in the

Department of Chemistry

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by

Arthur Katzakian, Jr.

June 1960

ACKNOWLEDGEMENT

The writer wishes to express his appreciation to the members of the faculty of the Chemistry Department of the College of the Pacific for their assistance during the period of study and especially to express his gratitude to Dr. Hugh Wadman and Dr. Emerson Cobb for their guidance and criticisms in this work.

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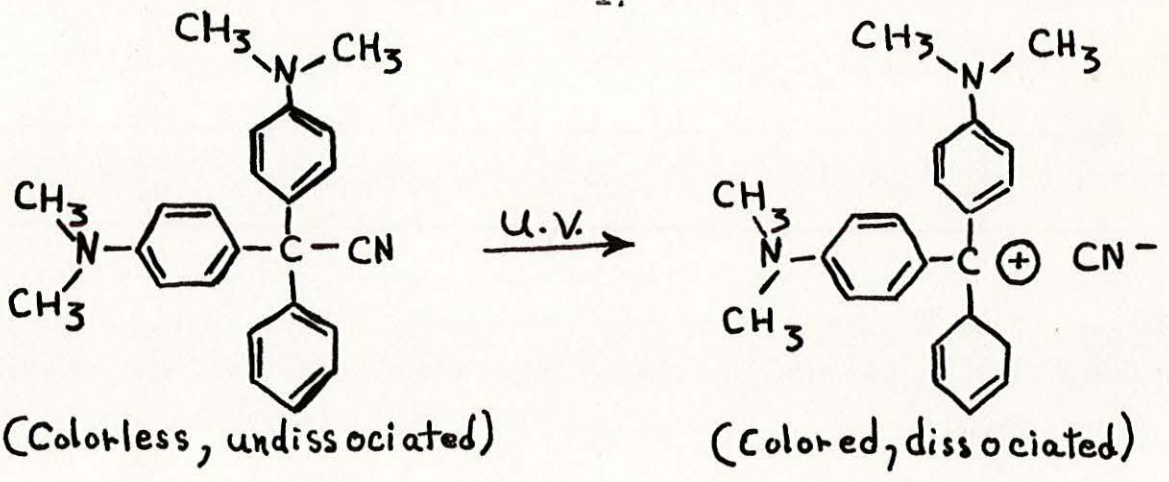
INTRODUCTION

In the field of actinometry there has existed a need for a suitable chemical actinometer. Although such an actinometer exists, the method of preparation is long, tedious and wasteful. There is also some question attendant upon various modes of behavior of this chemical actinometer. It is the purpose of this paper, therefore, to present a vastly improved method of preparation and attempt to promote more understanding of the mechanisms involved in this actinometry.

Harris and Kaminsky (10) made the first real contribution to the use of Malachite Green Leucocyanide (p,p'-di-dimethylaminotriphenyl acetonitrile) as a chemical actinometer. They showed that a quantum yield of unity was maintained by this actinometer for the spectral region between 3340 and 2480 Å. This photochemical reaction (I)

I.



is depicted as the ionization of the leucocyanide into p,p'-di-dimethylaminotriphenyl methyl ions and cyanide

ions yielding the exact color of the Malachite Green dye from which it was derived. The quantum yield of unity was not affected by temperature which further augmented the usefulness of this actinometer.

In a more recent paper Calvert and Rechen (1) verified the results of Harris and Kaminsky and showed that Malachite Green Leucocyanide was ideally suited to the measurement of very low light intensities, less than 10^{13} quanta/sec. They point out that although Uranyl Oxalate is used universally for the measurement of light intensities, its long exposure time, necessary at light intensities of 10^{13} quanta/sec. to achieve any degree of accuracy, is undesirable, thereby establishing the usefulness of the leucocyanide in this region. They did report, however, that above 10^{13} quanta/sec. the quantum yield became less than unity, presumably due to the absorption by the "photo compound" (p,p'-di-dimethylaminotriphenyl methyl ion).

As with other photo-sensitive materials these leucocyanides were studied for application to some phase of photography. The work by Konig (11) and Eder (3,4,5,) in attempting to apply the photo-oxidation process of the triarylmethane dye leucocyanides to photography proved unsuccessful. However, Eder did show these leuco bases to form films more light sensitive than dyed silver halide films which were previously used in the photometry of the visible region.

In the other extreme Chalkey (2) reported the compounding of x-ray sensitive papers with the leucocyanides

of Malachite Green and Pararosaniline. Ehrlich (6) stated that both papers were markedly affected when exposed to $5x10^6$ to 10^7 r. at 50 kv and 35 ma, but neither paper was affected in the lower dose range, thereby making it unlikely that these papers could ever be used for x-ray diagnosis, being essentially insensitive to x-ray of the medical diagnostic variety.

Malachite Green Leucocyanide was prepared in 1900 by Hantzsch and Osswald (8). Their method consisted essentially in dissolving the appropriate dye salt in water and adding it to a solution of potassium cyanide. The resultant highly colored precipitate was collected by filtration and subjected to a long series of extractions and recrystallizations which gave a very poor yield of leucocyanide still contaminated somewhat by the parent dye. Several attempts have been made since then to improve the procedure in making these leucocyanides (14,1). In both these cases the same problems arose, that of removing occluded dye from the precipitated leucocyanide. In the more recent attempt a yield of 56% of a product containing less than .001% dye and no trace of cyanide ion was reported. In all these cases the problem was attacked in the stage where the material had already precipitated and, hence, only involved the utilization of different solvents in the purification that required less overall time to remove the dye contamination. This procedure, however, was adaptable only to the class of basic triaryl methane dyes that showed water solubility.

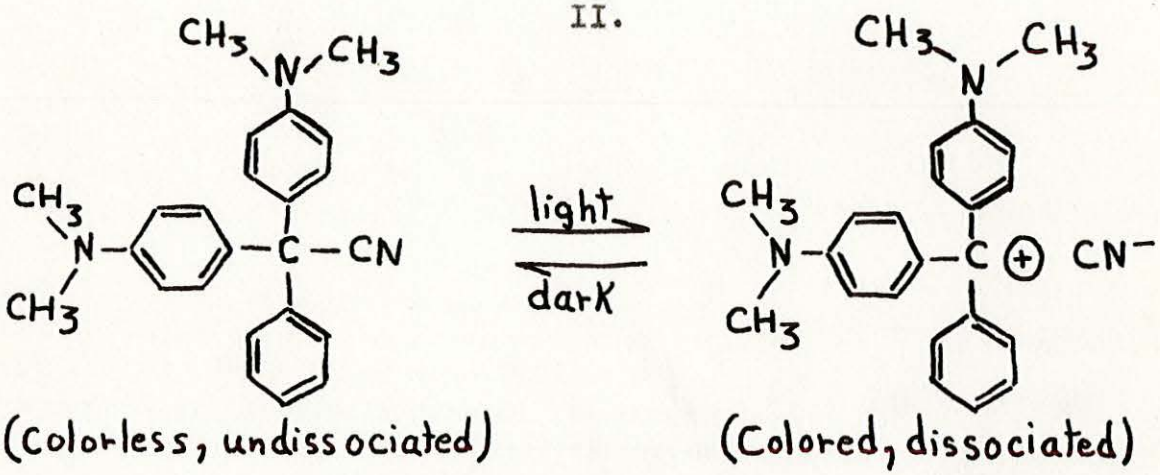
The ultra-violet absorption curves of the leucocyanides of Malachite Green and Crystal Violet dyes have been examined by Harris, Kaminsky and Simard (9). They also presented curves for the carbinol, the "photo compound" and the dye chloride; the latter two were also measured for spectra in the visible region. In the case of the Malachite Green, the leucocyanide and the leucocarbinol showed similar curves with their peaks slightly displaced from each other, the leucocyanide being at approximately 2720 Å and the leucocarbinol at 2680 Å. The "photo compound" and the dye chloride showed virtually the same curve for both the visible and ultra-violet regions. This property was similarly characteristic of the Crystal Violet group. No leucocarbinol was reported for Crystal Violet.

The dye and the "photo compound" of Crystal Violet showed a change in its absorption at 3130 Å when the solution was slightly acidified. A very marked change occurred in the visible region; the color shifted towards a green with the addition of acid. The same conditions for Malachite Green dye showed a slight broadening of its absorption band in the ultra-violet, but showed no observable change in the visible. This factor along with the greater solubility in alcohol of this leucocyanide made it more reliable as an actinometer and made 99.9% absorption possible with a shorter cell length than with that of the Crystal Violet Leucocyanide due to the solubility difference (10).

In the case of the Malachite Green Leucocyanide, a considerable amount of study has been placed on the phenome-

non of fading that it exhibits after photolysis, especially in 95% ethanol. Lifschitz and Joffé (14) proposed a mechanism for this fading that they felt applied to not only Malachite Green, but to Crystal Violet Leucocyanide as well. On the basis of a series of conductivity measurements of the photolyzed and unphotolyzed solutions they represented the reaction (II) as,

II.

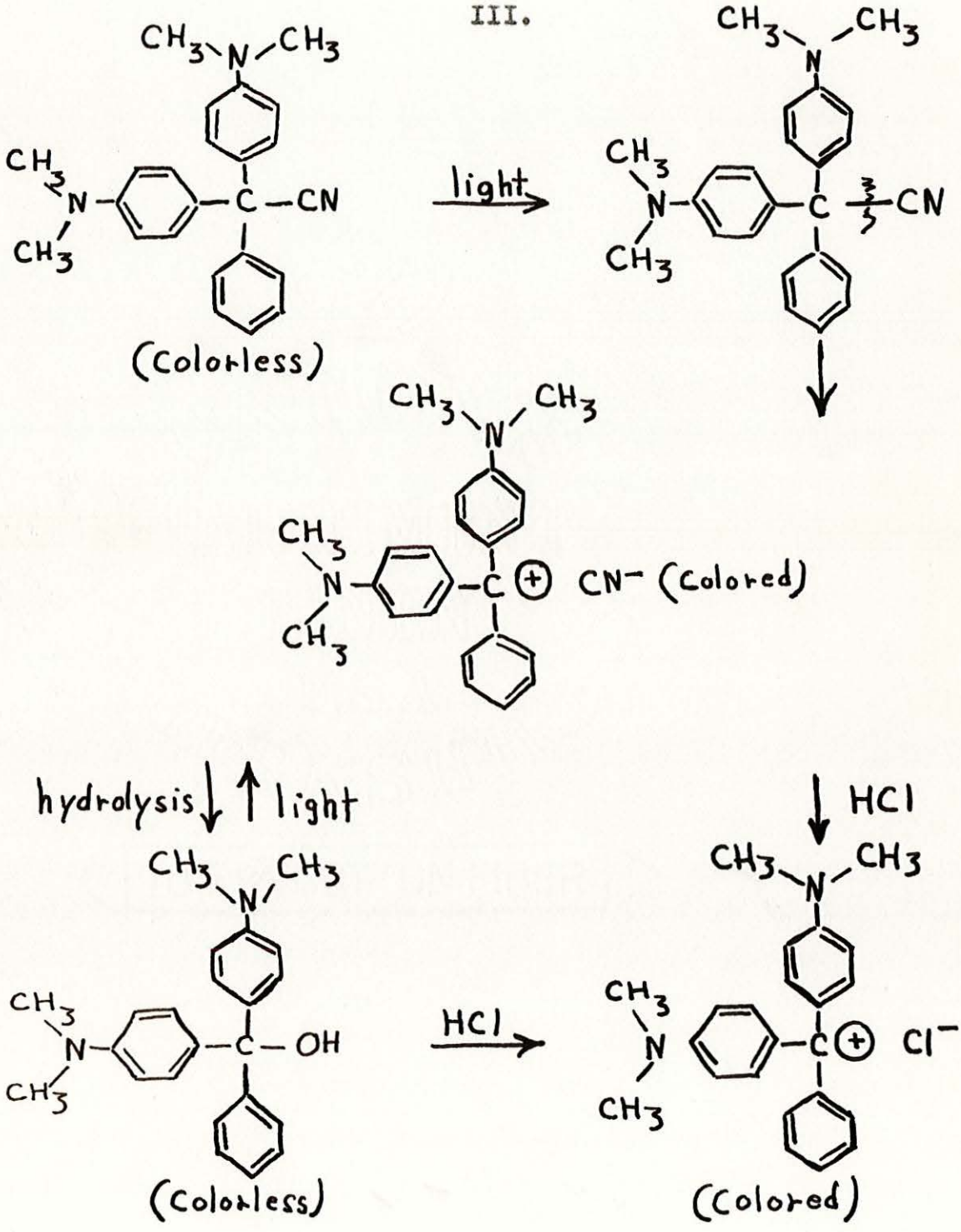


(Colorless, undissociated) (Colored, dissociated)

They assumed that solvolysis of the colored compound was of secondary importance. Harris, Kaminsky and Simard (9), however, found this explanation unsatisfactory for the behavior of the photolysis product of Malachite Green Leucocyanide. They found that the addition of water, potassium hydroxide and potassium cyanide accelerated the rate of color fading. No fading was observed with the addition of hydrochloric acid either before or after photolysis. The addition of hydrochloric acid to the partially decolorized photolyzed solutions essentially restored the color, but only 95-97% restoration was observed for water content greater than 20%. No coloration was observed if hydrochloric acid was added to the unexposed leuco-

cyanide solution. This indicated that the product of the observed fading in irradiated solutions of leucocyanides, not containing hydrochloric acid, was the colorless carbinol and not the original leucocyanide. On the basis of these observations the following mechanism (III) was proposed:

III.

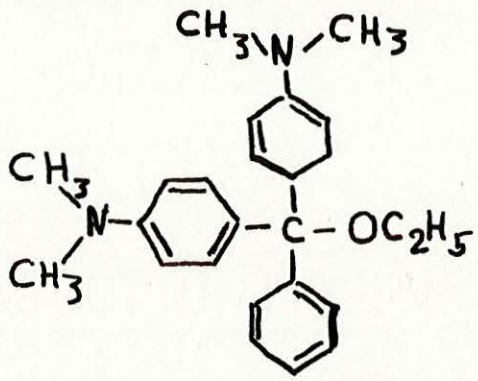


In view of this explanation, the effects of HCl, H_2O, KCN and KOH became evident. The fact that the colored product is regenerated upon reillumination of partially decolorized solutions is understandable when it is realized that the carbinol now undergoes photolysis, reproducing the colored compound. It was assumed that Reaction (1) was instantaneous; no intermediate compound was found for Reaction (1a). Reactions (2) and (4) are rapid and Reaction (3) is slow or moderate. The rate of fading had a positive temperature coefficient.

The most recent work in regards to the phenomenon of fading was done by Germann and Gibson (7). They investigated the ultra-violet absorption curve of a solution of Malachite Green Leucocyanide that was photolyzed for different periods of time and subsequently allowed to fade completely. They theorized that the absorption curves should shift from that of the leucocyanide to that of the leucocarbinol, depending on the time of irradiation. Such did not seem to be the case; they, in fact, reported the appearance of a new absorption band in the neighborhood of 3600 Å whose peak height seemed to depend on the time of irradiation. They concluded from this that there was a new end-product formed having the following properties: (a) It is colorless, but has a peak in its absorption curve in the region of 3600 Å. (b) It is formed more easily as the amount of water in the solution increases, but is unstable in as much as 15% water. (c) It is not as stable as the leucocyanide, being decomposed by dilute hydrochloric acid or excess water to form the

colored ion of Malachite Green. (d) When it is irradiated with ultra-violet light it generates the colored ion of Malachite Green. The following structure was proposed:(IV)

IV.



This structure is believed to form on interaction of the photolysis product with the ethanol (95%). It is to be expected that such a structure would be far more stable than was actually shown by experiment. The authors did recommend that further work be done to establish the true identity of the product resulting from fading. They reported that the original proposal by Lifschitz and Joffé (14) would be expected to hold in 100% ethanol.

The author deals first with the problem of preparation, since any quantitative study requires the isolation of a pure product. The problem was solved by using a solvent that was common to not only the reactants but to the product material as well, with ready miscibility with water. An attempt was made to prepare a diphenyl methane dye leucocyanide starting with Michler's Hydrol (bis-N,N-dimethylamino diphenyl carbinol). The hydrol was converted to the oxalate salt of the dye which was converted to the leucocyanide by

the procedure outlined by the author. The next phase of the work consisted in determining the ultra-violet absorption curves of six representative leucocyanides in an attempt to relate structure to peak absorption. A photolysis study was made for the same purpose. The final study concerned the phenomenon of fading exhibited by various leucocyanides after photolysis. Comparative fade rates were determined for Malachite Green Leucocyanide photolysis products in 95% ethanol, 99.5% acetone and 95% acetone. Ultra-violet absorption of the faded product in 95% ethanol was also determined.

EXPERIMENTAL RESEARCH

PREPARATION OF LEUCOCYANIDES

In 100 ml. of dimethyl sulfoxide were dissolved 5 g. of the appropriate triaryl methane dye. In an additional 25 ml. of dimethyl sulfoxide were dissolved 1.2 g. of NaCN. The dye solution was poured slowly with stirring into the NaCN solution and heated to a transparent yellowish solution. This solution was poured slowly with stirring into a liter beaker containing 200 g. water and 200 g. ice. The precipitate was collected by suction filtration and washed with cold water until the washings showed little or no cyanide contamination with $AgNO_3$ solution. The product was air dried. At this point the product was tinged with the color of the dye it was derived from due to residual ultra-violet light. It was further purified by dissolving in 100 ml. of a 50/50 mixture of acetone-water containing .1 g. of NaCN. The product crystallized out as a snow white material. It was collected by suction filtration, washed with 50 ml. of a cold 50/50 mixture of acetone-water and air dried. The product was stored in a brown bottle.

Although the above procedure was used in the preparation of all the leucocyanides, modifications were made based on the impurity of the initial dye salt. In the very impure cases, the product obtained from dimethyl sulfoxide was dissolved in 300 ml. of a .1N HCl solution and treated with 5 g. of activated charcoal for four hours. The charcoal

was removed by filtration and the clear filtrate was made alkaline with conc. NH_4OH. The product was filtered by suction, washed with water and dried. It was further purified by the above method.

In some instances in the final purification the product was observed to darken and form an oily, low-melting mass when the solution was heated near its boiling point. In this case the product was not dissolved in the acetone-water mixture, but was subjected to heavy shaking to dissolve out the impurities. This behavior was observed only with the compounds that have aryl groups substituted on the terminal amines. Although the breakdown product was not identified, it is believed the break occurs at the point where the aryl groups are substituted on the amines, because the resultant product resembles an oil similar to benzene or aniline. It is not practical at this point to attempt to purify this mass. An attempt was made at this point to make a leucocyanide of a diphenyl methane dye.

In a solution of 150 g. oxalic acid in 300 ml. water were dissolved 50 g. of Michler's Hydrol (bis-N,N-dimethyl amino diphenyl carbinol). The solution was diluted with 150 ml. of water, heated to 65° C. and filtered. The filtrate was poured into a copper pan and allowed to sit for one week. The dye crystals were filtered with suction, dried and converted to the leucocyanide by the method outlined above.

FIG. I.

LEUCOCYANIDES PREPARED BY METHOD OF AUTHOR
WITH RESPECTIVE MELTING POINTS AND YIELDS[1]

Color Index No.	Dye	Melting Point	Yield
657	Malachite Green	178-179° C.	4.4g.(92.4%)
658	Rhoduline Blue 6GA	197-198° C.	1.5g.(31.2%)
662	Brilliant Green	159-160° C.	3.2g.(75.1%)
676	Pararosaniline	242-244° C.	4.0g.(82.2%)
677	Magenta XX	249-250° C.	3.6g.(70.2%)
678	Magenta ABN	249-250° C.	3.0g.(58.5%)
679	Dahlia	181-182° C.	4.0g.(81.2%)
680	Methyl Violet	254-255° C.	3.6g.(73.5%)
681	Crystal Violet	289-290° C.	3.5g.(71.7%)
682	Ethyl Violet	224-225° C.	3.9g.(79.2%)
689	Spirit Blue	185-186° C.	1.5g.(31.2%)
690	Victoria Blue 4R	159-161° C.	2.0g.(41.4%)
728	Victoria Blue R	250-251° C.	4.2g.(85.4%)
731	Night Blue	239-240° C.	2.5g.(50.7%)

1. These yields are based on the quantity of crude dye used.

ULTRA-VIOLET ABSORPTION AND PHOTOLYSIS STUDY

Alcoholic (95%) solutions of Malachite Green, Brilliant Green, Pararosaniline, Crystal Violet, Victoria Blue R and Victoria Blue 4R leucocyanides of 5×10^{-6} M were prepared and their absorption curves in the ultra-violet region were determined on a Beckman Model DU Spectrophotometer.

In order to prevent absorption by the "photo compound", a continuous flow apparatus was used. This consisted of a 250 ml. separatory funnel as the reservoir which was connected to the cell by means of capillary plastic tubing. The cell compartment cover was replaced with black cardboard through which the tubing passed. The flexibility of the tubing allowed the cell to be moved back and forth without difficulty. A second tubing was used as a drain. This setup insured a continual renewal of the leucocyanide solution.

These same solutions were subjected to ultra-violet irradiation with a mercury arc lamp to compare apparent rate of color formation in each case. The comparison was made visually because intense monochromatic ultra-violet light in the appropriate region was not abailable. The solutions were made slightly acid and again irradiated with ultra-violet light.

FIG. II.

ULTRA-VIOLET ABSORPTION OF MALACHITE GREEN LEUCOCYANIDE

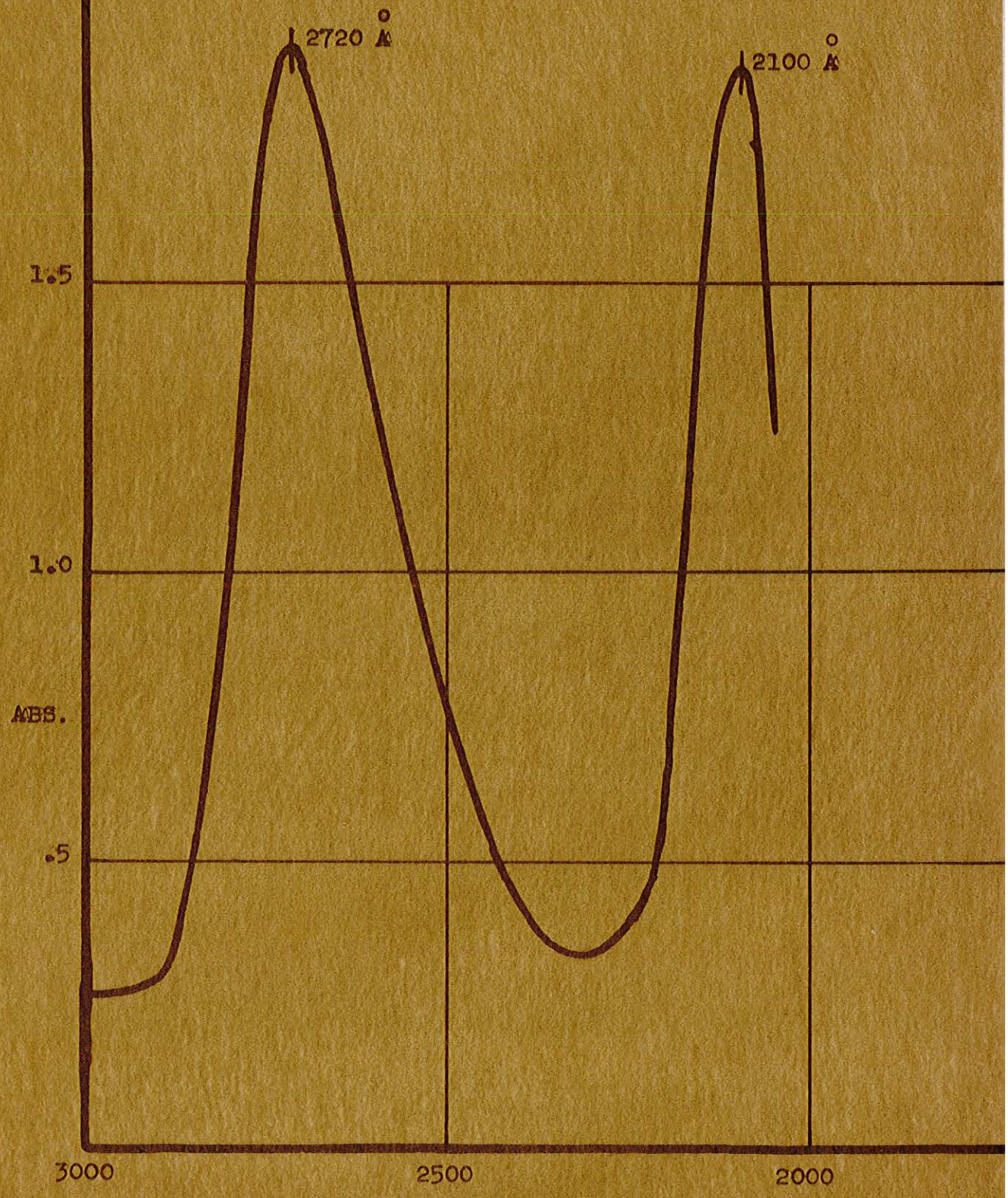


FIG. III.

ULTRA-VIOLET ABSORPTION OF BRILLIANT GREEN LEUCOCYANIDE

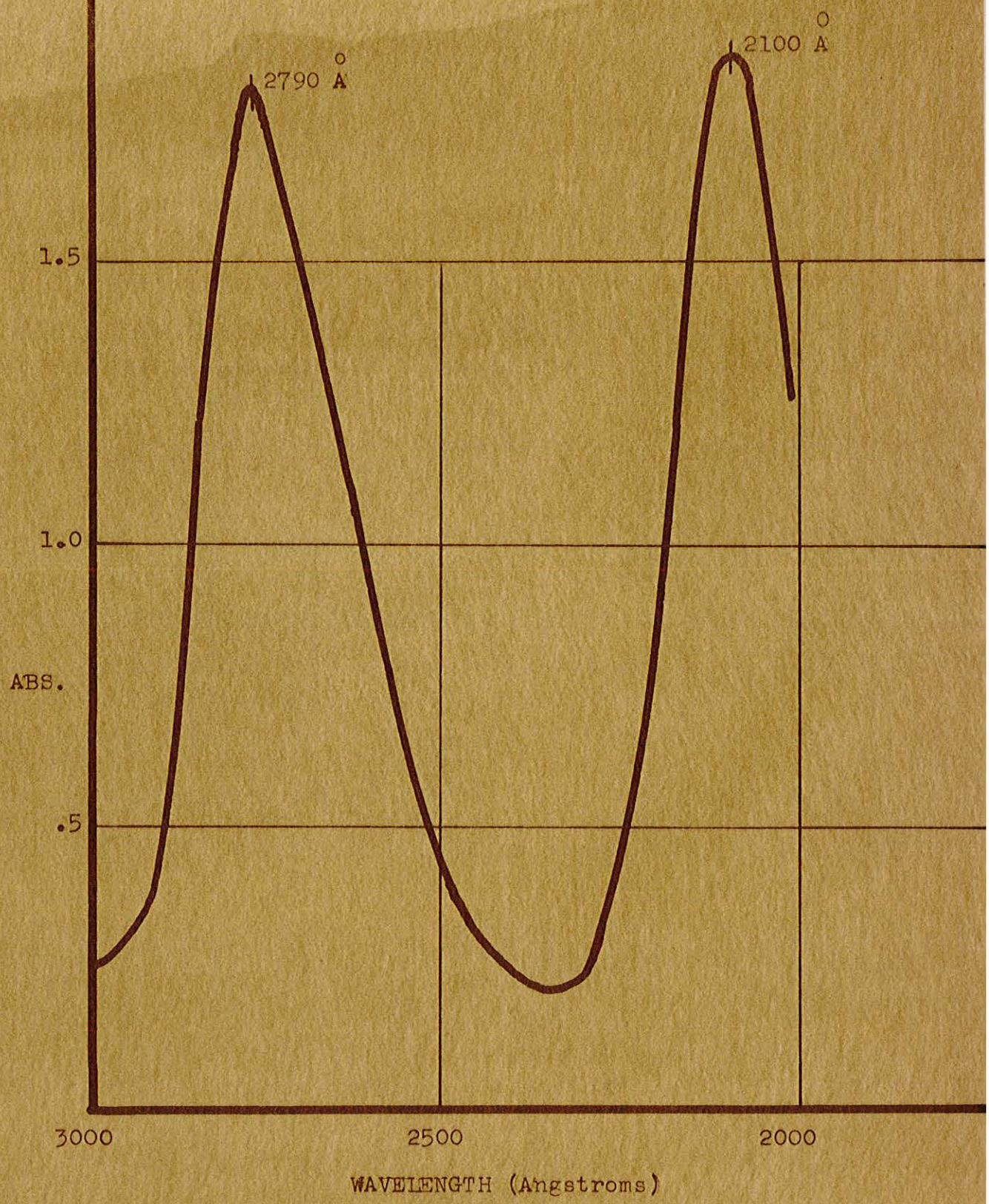


FIG. IV.

ULTRA-VIOLET ABSORPTION OF PARAROSANILINE LEUCOCYANIDE

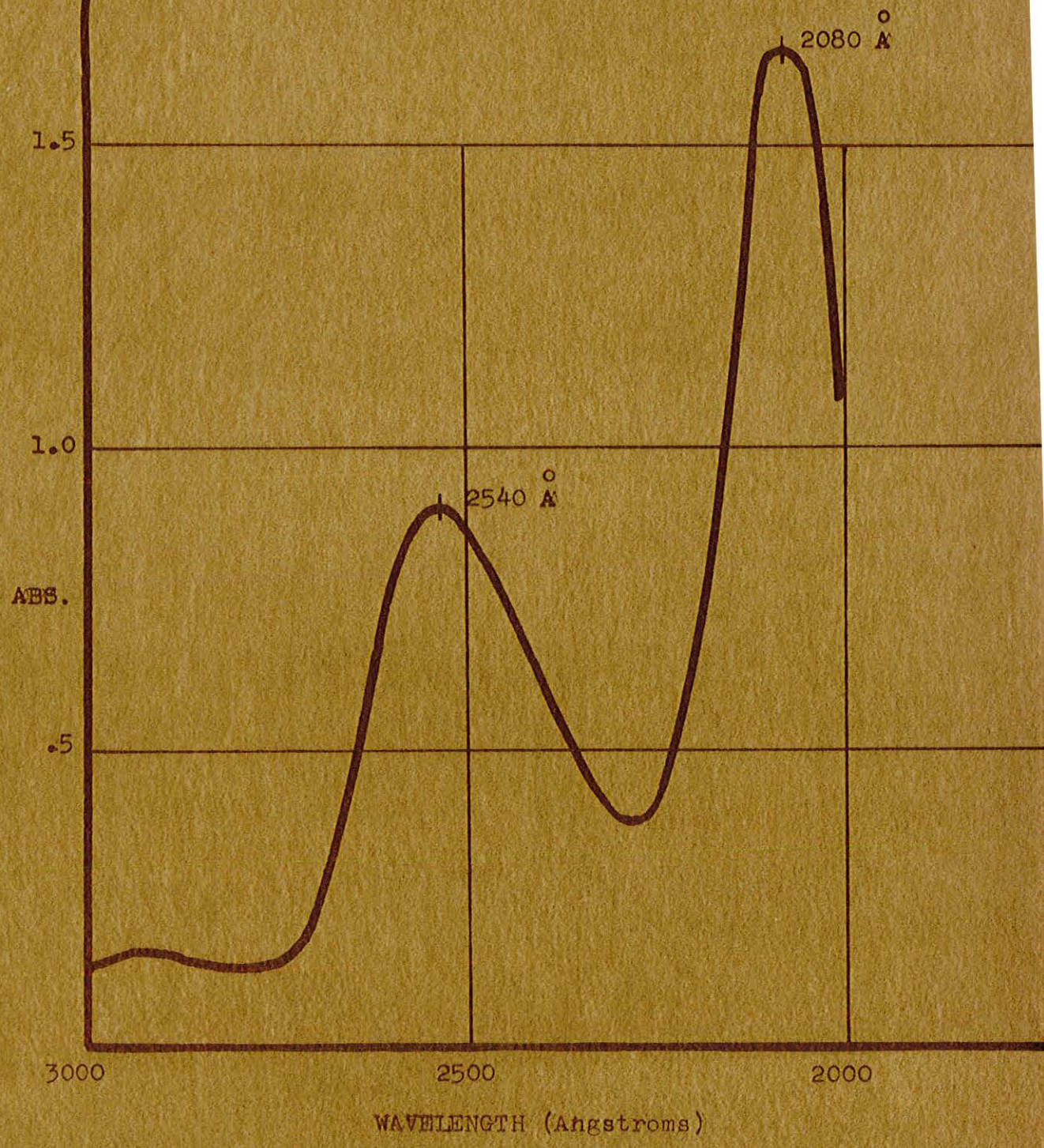


FIG. V.

ULTRA-VIOLET ABSORPTION OF CRYSTAL VIOLET LEUCOCYANIDE

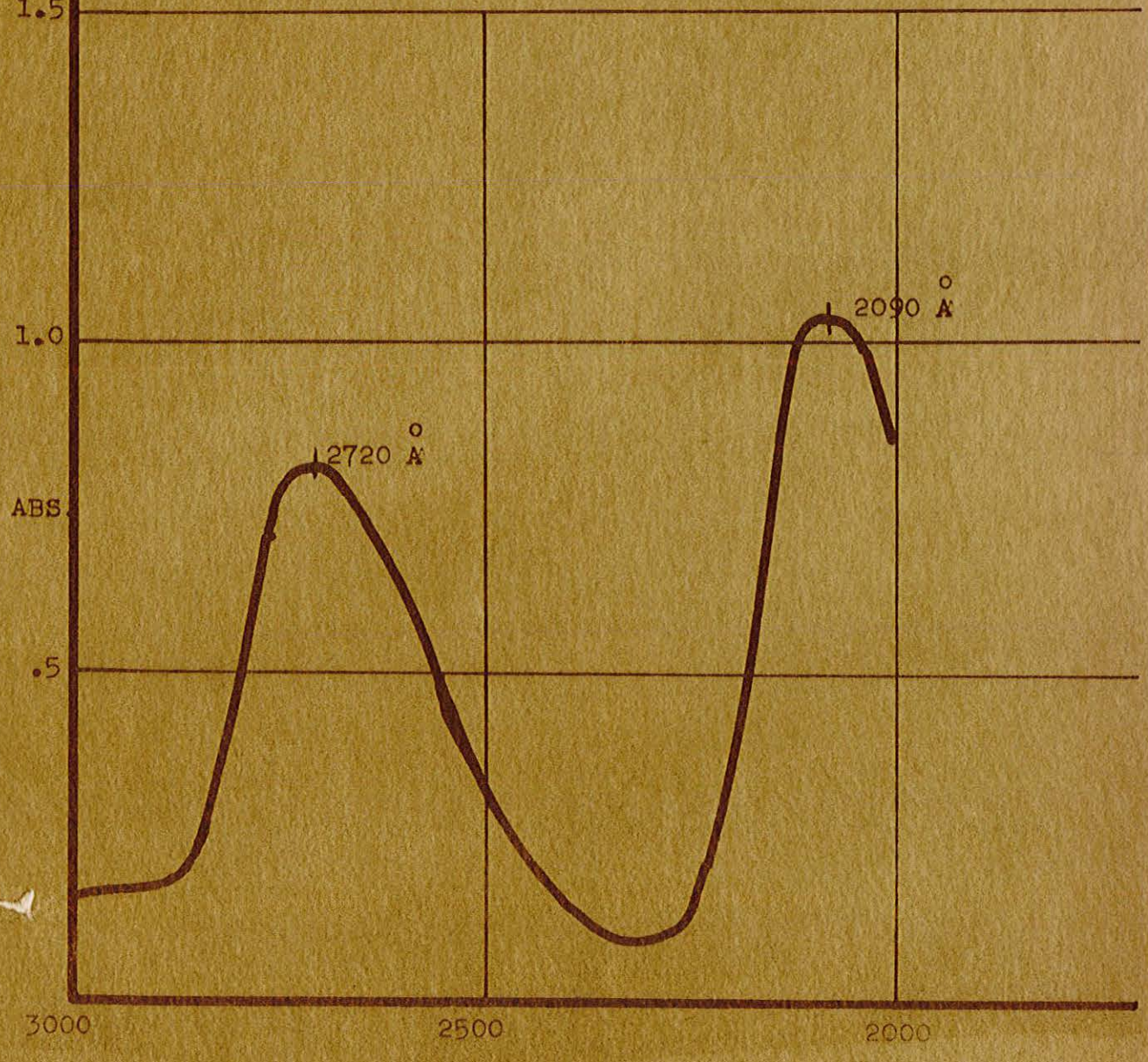


FIG. VI.

ULTRA-VIOLET ABSORPTION OF VICTORIA BLUE R LEUCOCYANIDE

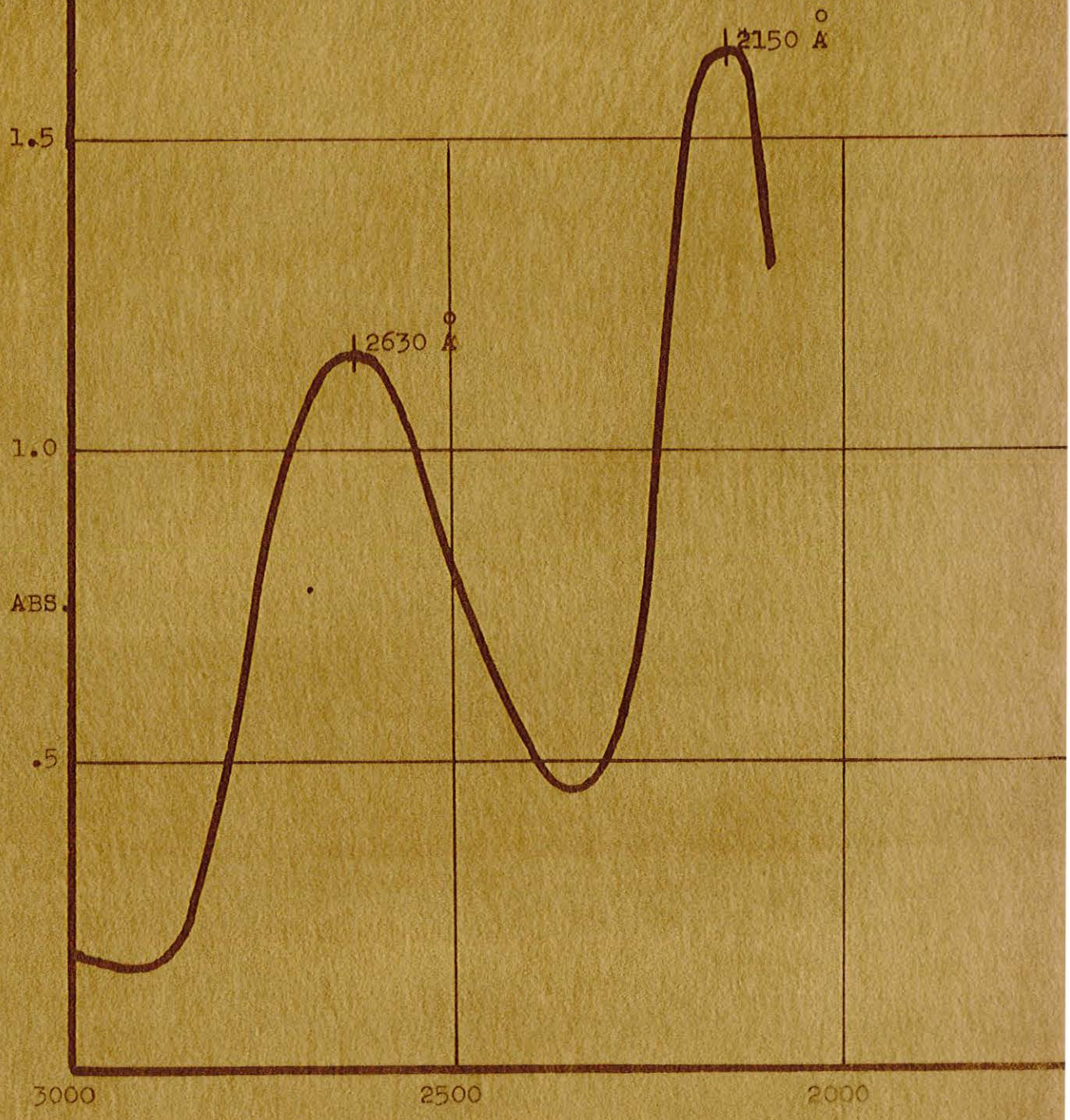
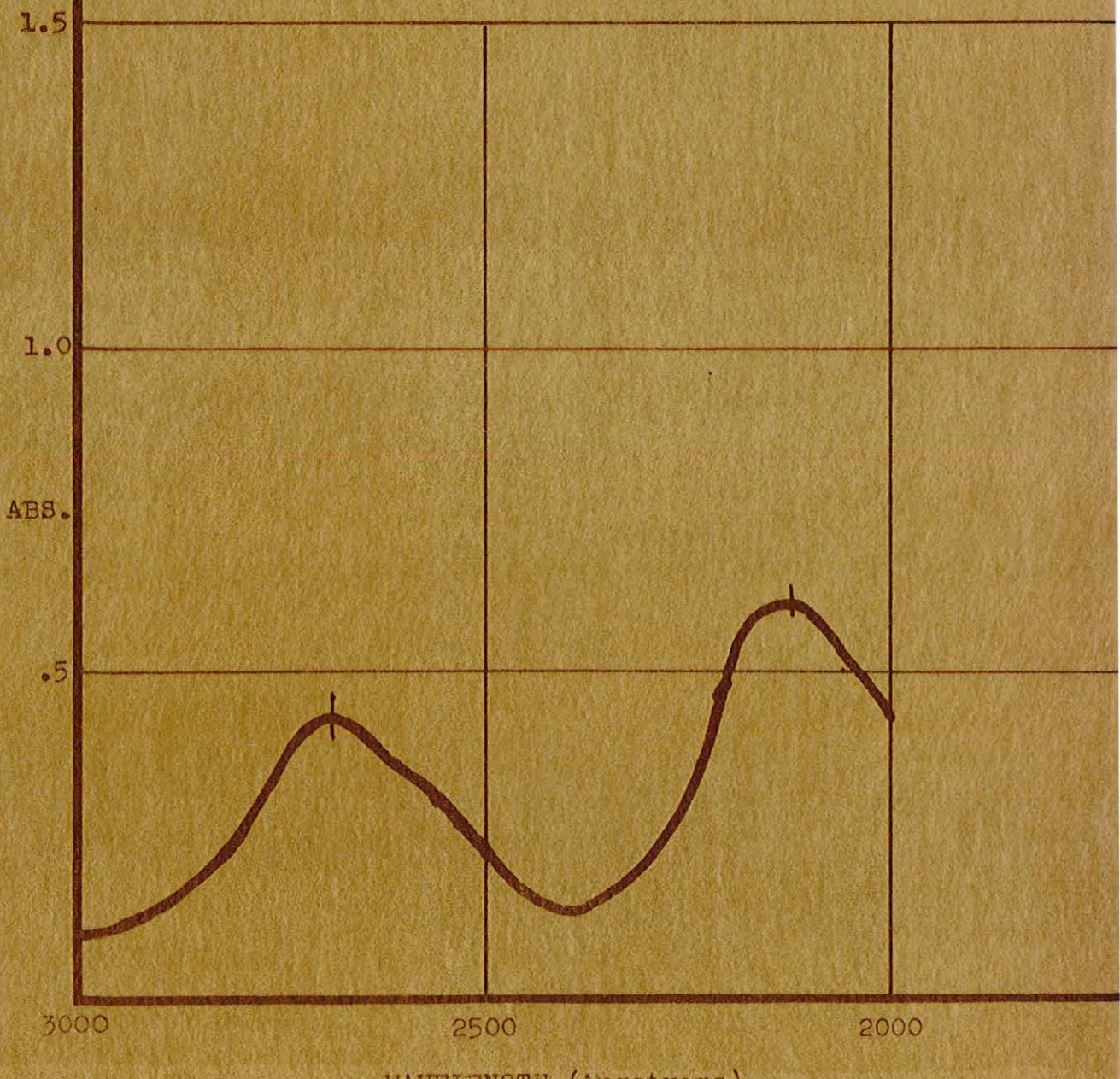


FIG. VII.

ULTRA-VIOLET ABSORPTION OF VICTORIA BLUE 4R LEUCOCYANIDE



INVESTIGATION OF FADING RATES

100 ml. of an alcoholic (95%) solution of Malachite Green Leucocyanide containing .686 g. was prepared. An additional 100 ml. of solution was prepared at the same strength using acetone as the solvent. The two solutions were subjected to a mercury arc lamp for two hours. At the end of such time 2 ml. of each of these solutions was diluted to 11 ml. with pure solvent and read for transmittance at 6200 $\mathring{A}$ on a Coleman Jr. Spectrophotometer. This procedure was repeated every fifteen minutes. The final solutions were acidified with a drop of conc. HCl and 5 ml. of the solutions each were diluted to 11 ml. with pure solvent and read for transmittance at the same wavelength.

An additional solution of the same strength was prepared using 95% acetone as the solvent. This solution was subjected to ultra-violet irradiation for two hours and allowed to fade completely. Its transmittances were measured in the same manner as above.

10 ml. of the original faded alcoholic solution (2×10^2 M) was pipetted into a 100 ml. volumetric flask and diluted to the mark with 95% ethanol. A second solution was prepared using 2.5 ml. of the original solution diluted to 100 ml. The first of these two solutions was measured for ultra-violet absorption in the region of 3700 $\mathring{A}$ to 3300 $\mathring{A}$. The second solution was measured from 3100 $\mathring{A}$ to 2100 $\mathring{A}$. The spectra were run on a Beckman Model DU Spectrophotometer.

FIG. VIII.

FADE RATE STUDIES OF PHOTOLYZED SOLUTIONS OF MALACHITE GREEN LEUCOCYANIDE (2×10^{-2}M) AT 6180 Å.

Time inter. min.	ETHANOL (5% water) % Trans.	Acetone (.5%) % Trans.	Acetone (5%) % Trans.
0	36.0	32.2	19.0
15	78.8	35.3	25.0
15	84.2	36.5	29.0
15	90.6	37.5	32.5
15	93.6	37.8	34.0

FIG. IX.

ULTRA-VIOLET ABSORPTION OF BACK REACTION PRODUCT OF MALACHITE GREEN LEUCOCYANIDE (2×10^{-5}M) IN 95% ETHANOL IN REGION OF REPORTED APPEARANCE OF ABSORPTION PEAK.

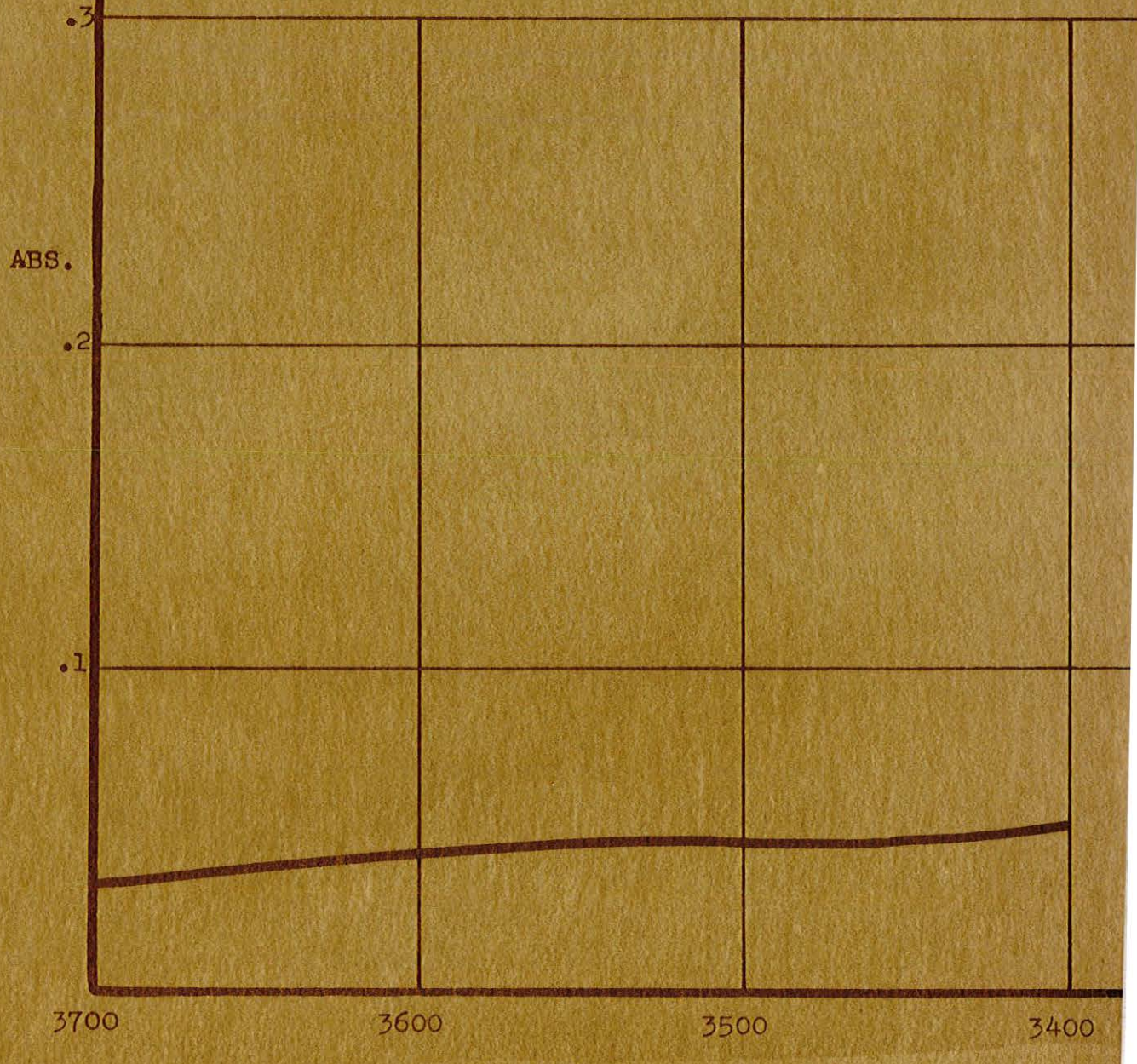
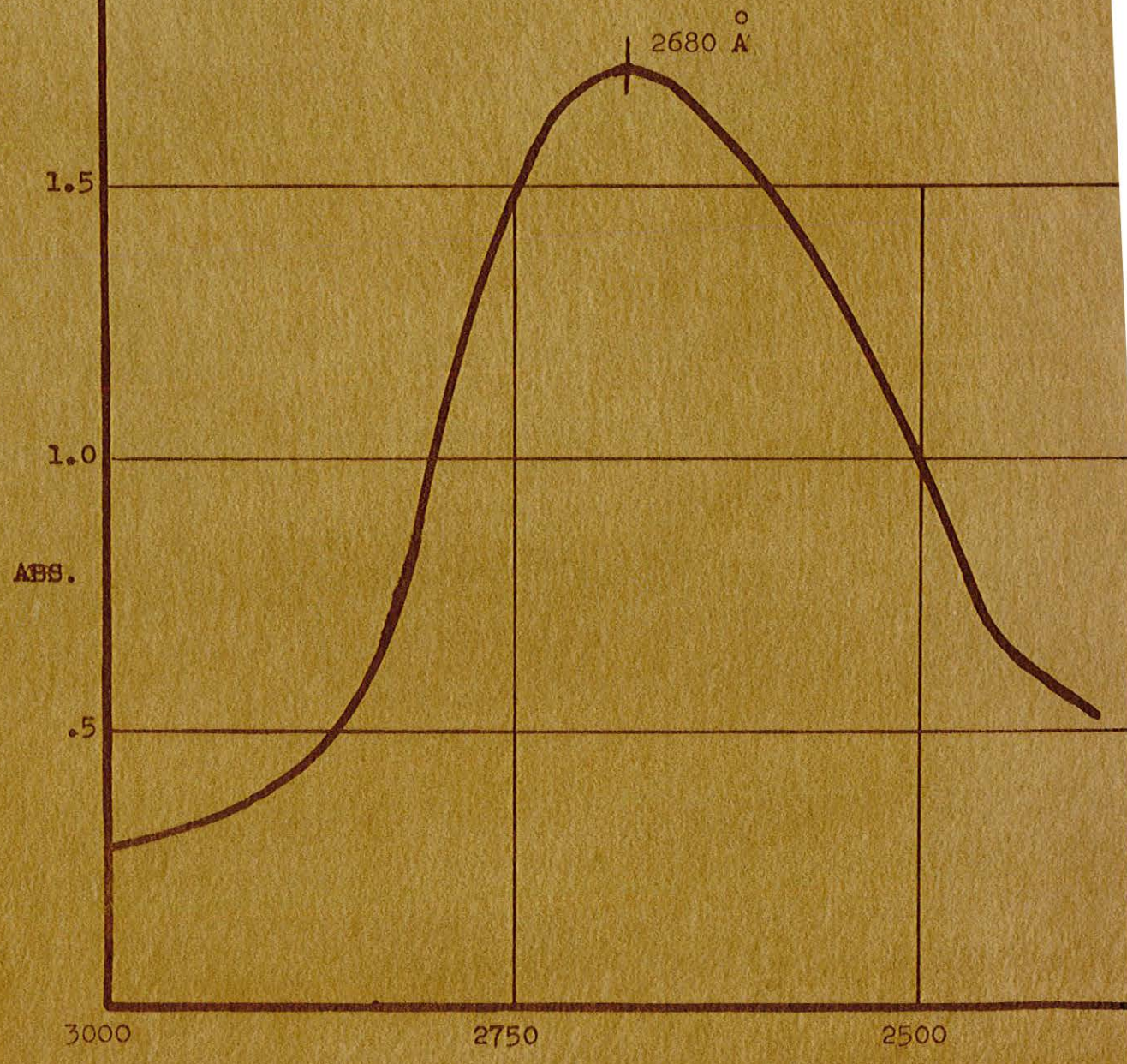


FIG. X..

ULTRA-VIOLET ABSORPTION OF BACK REACTION PRODUCT OF MALACHITE GREEN LEUCOCYANIDE (5×10^{-6}M) IN 95% ETHANOL.



DISCUSSION OF RESULTS

Thirteen triarylemthane dyes were converted to their respective leucocyanides. (FIG. I.) The melting points of the leucocyanides reported in the literature were essentially the same as the corresponding leucocyanides reported here. Mixed melting points with Malachite Green Leucocyanide prepared by both methods showed no depression. All the leucocyanides were stable to strong acids as opposed to the ready conversion of the carbinol derivatives of the dye back to the dye.

The yields reported here were based on the initial amount of dye used, which in most cases were somewhat less than 100% pure. The indication in the case of Malachite Green is that the yield is essentially 100% and any loss is purely mechanical.

The results indicate that the outlined procedure is quite satisfactory and more desirable than previous methods of preparation. By being able to keep the product and reactants all in solution together it becomes possible to drive the reaction to completion in the initial step. This makes it unnecessary to use involved recrystallization and extraction techniques to remove occluded dye.

The product is essentially free from cyanide contamination and residual dye color, resulting in solutions that are colorless even when made slightly acid.

The drawback to this procedure, as well as any of the preceding ones, is that the ultimate yield depends on the

initial purity of the dye crystal. Although the more widely used dyes as Malachite Green Oxalate and Crystal Violet Chloride are obtainable in essentially 100% purity, the bulk of the basic triarylmethane dyes are not. These are generally made just pure enough for staining of biological specimens.

An attempt was made to synthesize the leucocyanide of a diphenylmethane dye to determine what effect this would have on the absorption and activating wave length with the idea or purpose of discovering the role that the structure played in absorbing Ultra-Violet and effecting the dissociation of the leucocyanide. A brown product was obtained, but in insufficient amount to be properly purified.

All the leucocyanides exhibited two characteristic absorption peaks, the first of which occurred within 200 Å of each other. The second peaks occurred in a much tighter band, having a spread of approximately 80 Å. In all instances except for Malachite Green Leucocyanide, the peaks are very nearly equal in height. (FIG. II. - VII.)

By comparing the curves with their respective molecular structures it appears that the first absorption peak is characteristic of these substitution groups on the amino nitrogens. There does not seem to be any clear cut pattern that applies to all cases. However, if we were to exclude Malachite Green Leucocyanide and compare the first curves of the triamino triaryl methane leucocyanides we would see that as the substitution groups on the amines became smaller,

the peaks were displaced to shorter wavelengths. For example, Pararosaniline, whose amines are all primary, has its peak at the shortest wavelength and crystal violet, whose amines are all substituted with methyl groups, has its peak at the longest wavelength.

By the same token, it is believed that the second peak is characteristic of the triaryl methane nucleus of the dye. In all cases except that of Victoria Blue R Leucocyanide, the peaks are all approximately at 2100 Å. The Victoria Blue R, having a larger nucleus has its second peak displaced towards a longer wavelength.

The leucocyanide that was synthesized (bis-p,p'-dimethyl-amino diphenyl aceto nitrile) was not prepared in sufficient purity to check its melting point or absorption curve, but an alcoholic solution was checked under a mercury arc lamp for ultra-violet sensitivity. It showed ultra-violet sensitivity, but only after the lamp had developed its shortest wavelength emission. A blue color developed which appeared to be the same as the original dye color. This leucocyanide showed the characteristic stability to acids shown by all the other leucocyanides.

The procedures used for the preparation of the parent dyes to these leucocyanides were essentially that for making malachite green oxalate; Most of the product was lost at the stage where the dye salt was crystalized. This salt was quite impure and attempts to prepare the leucocyanides from them resulted in a very small yield of crude product. Efforts to purify this product only resulted

in its near complete loss. Consequently, absolute identification was not feasible, but general characteristics did show more than coencidental similarities to the other leucocyanides.

It appears that the two absorption peaks of the leucocyanides in the ultra-violet region characterize first the various substituted amines and secondly the nucleus of the structure. The photolysis of Malachite Green Leucocyanide for the determination of the quantum yield has been carried out in the region of 2482 $\mathring{A}$ to 3342 $\mathring{A}$ and found to be one. This signifies that the activating wavelength does not have to lie within the confines of the peak absorption. It would be desirable at this point to know whether or not ultra-violet light of 2100 $\mathring{A}$ would have an activating effect on the molecule. The absorptions have been shown to be as great if not greater at 2100 $\mathring{A}$ than at the other peaks.

The diphenyl methane leucocyanide showed apparent absorption in the very short wavelength region of the ultra-violet light due to its slow color formation at the mercury arc lamp peak output. It is only in the formation of the dye crystal that needs refinement before a suitable amount of leucocyanide of this dye can be obtained in reasonable purity. An absorption curve in the ultra-violet of this leucocyanide can possibly prove to be very illuminating. All the leucocyanides showed photolysis in the presence of acid.

The fade rate studies of Malachite Green Leucocyanide show the fastest fading for the alcoholic (95%) solution.

The rate is markedly increased in acetone with the addition of water. (FIG. VIII.) Although hydrolysis plays the major role in the fading of the photolysis product it is believed that the reformation of the original leucocyanide competes. This is based on the observed fact that the acidified final solutions showed, in the case of the alcohol (95%), a one percent transmission and, in the case of the acetone (99.5%), an eight percent transmission. The fact that the acidified portions showed far less transmittance can be explained by the fact that when water is present an equilibrium is set up between the photolysis product and the back reaction product such that the color density does not increase appreciably after a certain point is reached. Consequently, a reserve of the carbinol is built up which only shows itself when the solution is acidified.

Although the evidence is not conclusive, it is believed to be sufficient to show that the "back reaction" product is the carbinol and not some other linkage as proposed by Germann and Gibson (7). The linkage in the acetone is too stable to be attacked by such a mild reagent as the dye ion. Furthermore, Germann and Gibson reported that the reformation of the original leucocyanide was quite probable in 100% ethanol. If this be the case, the formation of an ether linkage with the ethanol in the 95% solvent would appear to be contradictory, because one would expect this reaction to be enhanced in 100% ethanol, not diminished.

The author failed to show the appearance of a new

absorption band in the region of 3600 Å for the back reaction product. Instead, the absorption shifted as would be expected to that of the leucocarbinol. (FIG. IX-X.) A desirable way to prove conclusively what this back reaction product is would be to analyze the faded solution chromatographically and compare it to chromatograms of the pure leucocyanide and the pure leucocarbinol. A suitable solvent system would have to be developed that excludes water, for none of these leuco compounds exhibit water solubility.

SUMMARY

The author has developed a procedure that applies generally to the preparation of the leucocyanides of the basic triaryl methane dyes. The ready availability of such a vast number and variety of leucocyanides should enhance the use of these compounds in the field of actinometry. The absorption in the ultra-violet of six representative members of this group has been run and compared to the structure of its parent leucocyanide. It was shown, although not conclusively, that the first peak corresponded to the size and nature of the chromophoric groups and the second peak was characteristic of the triaryl methane nucleus.

A partially successful attempt was made to synthesize a diphenyl methane leucocyanide. The compound showed limited sensitivity to ultra-violet light, presumably in the very short wave length region.

Fading rates were run on photolyzed solutions of Malachite Green Leucocyanide both in ethanol and acetone. The fading in acetone was accelerated when water was added, showing hydrolysis to be of primary importance in the fade rate. Absorption curves in the ultra-violet of the faded solution showed no absorption in the region of 3600 Å and exhibited a shift in absorption peak to that of the carbinol.

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